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Intramolecular versus intermolecular mechanism of metallotropic rearrangements of chiral chromium tricarbonyl complexes of substituted naphthalenes and other polyaromatic compounds investigated by chiral HPLC of its racemic mixtures

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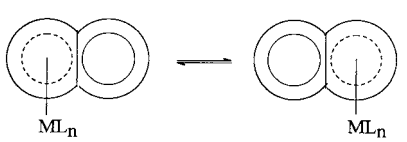
Abstract

Pure enantiomers of chromium tricarbonyl complexes of α- and β-monosubstuted naphthalenes R–$C_{10}H_7Cr(CO)_3$ (R = Cl, Me, $SiMe_3$, $SnMe_3$) were separated as pure enantiomers by chiral phase HPLC on a Chiracel OD column. Inter-ring haptotropic rearrangements (IRHRs) (process in which metal shifts between substituted and non-substituted rings) of pure enantiomers were investigated in different solvents in the presence or absence of some solvating additives. It was shown that IRHR proceeds at 85°C in noncoordinative and noncomplexing solvents such as hexafluorobenzene or decane through an intermolecular mechanism without racemization. In aromatic toluene, which can bind with the organometallic group, it proceeds through a partially intramolecular mechanism, leading to considerable racemization (ca. 20%) of the complexes. In the presence of solvating additives (THF, dibutyl ether), almost complete racemization (> 90%) was observed.

Keywords: Metallotropic; Chromium tri(carbonyl) aromatic; Chiral HPLC

1. Introduction

π-Complexes of transition metals with unsaturated or aromatic ligands, in which the metal binds only some of the accessible ligand coordination sites, are quite labile and characterized by different dynamic processes. Among the most thoroughly studied reactions are inter-ring haptotropic rearrangements (IRHRs). Here the metal migrates from one position of the ligand to another (Eq. (1)). These processes were thoroughly investigated for chromium tricarbonyl complexes of fluorenyl and indenyl anions [1], as well as for their heterocyclic analogs [2], substituted biphenylenes [3], biphenyls [4] etc.



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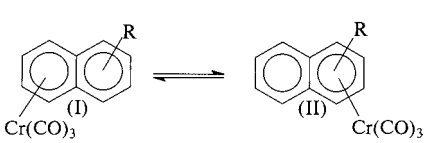
Kinetic and thermodynamic parameters of a number of IRHRs, particularly for chromium tricarbonyl complexes of substituted naphthalene containing substituent-label R in non-coordinated (**I**) or coordinated (**II**) rings, were determined by means of NMR spectroscopy (Eq. (2)) in different solvents [5–7], and theoretically by extended Hückel [8] and DFT [5] methods. However, to date the mechanism for this reaction is not completely clear.



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Three plausible mechanisms exist for such a rearrangement:

1.1. Dissociative

In the course of this mechanism chromium tricarbonyl group loses its bond with the aromatic ring in the ligand and moves into the solvent phase.

It is reasonable to assume that in a solvent $Cr(CO)_3$ forms a complex of the type $(solvent)_nCr(CO)_3$ (Eq. (3)). Such a mechanism is quite probable in polar heteroatom-containing (THF, ethers, pyridine, solvating additives) or in aromatic (benzene, toluene) solvents (Eq. (3)) that can form σ- or π-complexes with the chromium tricarbonyl group (e.g. $Py_3Cr(CO)_3$ or η^6-$areneCr(CO)_3$), respectively. These exchange reactions are quite common at elevated temperatures ($\geq 100°C$). For example, THF is found to be a good solvent or solvating additive for the synthesis of chromium tricarbonyl complexes of different polyaromatic arenes, either from $Cr(CO)_6$ [6] or from η^6-naphthalene-$Cr(CO)_3$ [9], due to its ability to produce the labile intermediate $(THF)_3Cr(CO)_3$, which further affords 'hot' $Cr(CO)_3$ particles randomly attacking different rings of arenes. The existence of this unstable $(THF)_3Cr(CO)_3$ complex was proved by means of IR spectroscopy [10]. It was shown that the transfer of the chromium tricarbonyl group from the naphthalene complex to toluene at elevated temperatures proceeds quite easily in hydrocarbon solvents [11], whereas such a transfer to benzene can be characterized by the rate constant $k_{exch.} = 1.73 \times 10^{-4}\ s^{-1}$ at 140°C [9].

1.2. Intramolecular

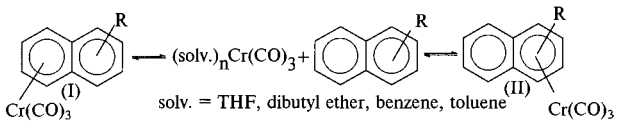
The intramolecular mechanism takes place when in the course of IRHR the chromium tricarbonyl group shifts along the plane of the π-ligand without loss of coordination to the arene molecule.

This is particularly true with aliphatic solvents (decane, decaline) or C_6F_6. In our previous investigation we demonstrated that C_6F_6 was a very convenient solvent for the investigation of IRHR due to the high solubility and stability of the complexes in this solvent and a low probability of the formation of chromium tricarbonyl complexes with C_6F_6 [5].

1.3. Bimolecular

The bimolecular mechanism assumes the exchange reaction of $Cr(CO)_3$ groups between two molecules of arene chromium tricarbonyl complexes occurs.

This mechanism seems to be less probable for IRHR in substituted naphthalenes due to the fact that the second six-membered ring in the molecule of the corresponding chromium tricarbonyl complex has only four π-electrons, so it can hardly coordinate the second $Cr(CO)_3$-group. Nevertheless, such a mechanism has been discussed by Trailor et al. [12] for the description of ligand exchange reactions of chromium tricarbonyl complexes of different arenes.



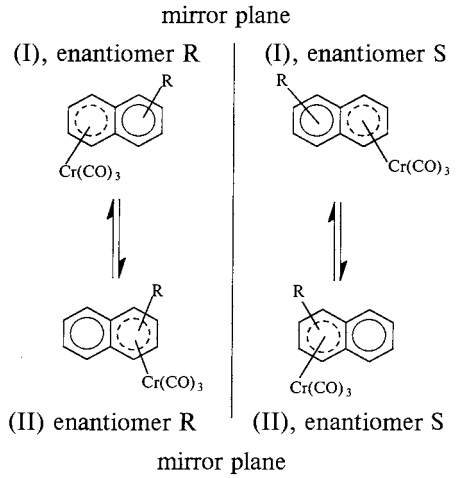
(3)

Chiral organometallic compounds are considered as useful reagents in the asymmetric synthesis of organic compounds of high stereoselectivity and in asymmetric catalysis [13]. This greatly increases the interest in optically active organometallic compounds [14]. Recently, many advances have been made in the separation technology of enantiomers of organometallic π-complexes by chiral phase HPLC [15–18]. In particular, chromium tricarbonyl derivatives of substituted polyaromatic hydrocarbons (PAH), which have planar chirality and can be separated by HPLC [15,16]. To our knowledge, only a few papers dealing with the use of enantiomers of organometallic complexes for the investigation of the reaction mechanisms have been published [19,20].

The investigation of the racemization of enantiomers of chromium tricarbonyl complexes of arenes could provide valuable information concerning the IRHR mechanism. For this purpose a number of enantiomers of chromium tricarbonyl complexes of substituted naphthalenes [5], separated by chiral phase HPLC, were incubated at an elevated temperature in an inert solvent, C_6F_6, with low coordination ability, as well as in an aromatic solvent, toluene. Depending on the type of mechanism one can observe different reaction products. In the absence of bond cleavage during IRHR (intramolecular mechanism), only one additional chromatographic peak related to a positional isomer of the same original enantiomer should appear. Conversely, the dissociative intermolecular mechanism supposes the loss of optical activity or racemization in the course of IRHR, which means the appearance of four chromatographic peaks on the chromatogram (Scheme 1).

2. Results and discussion

Modified cellulose carbamate adsorbed on silica as chromatographic supports were developed by the group of Okamota [21] and are now available from Daicel (Japan) under the trade name Chiracel. A variety of chromatographic columns of this type having different substituents in the phenyl rings of the carbamate moiety are now available. Chiracel OD was selected here (arene ring is 3,5-dimethyl substituted, Fig. 1), as it had been previously used for the separation of the enantiomers of chromium tricarbonyl complexes [16].



Scheme 1.

previously used for the separation of the enantiomers of chromium tricarbonyl complexes [16].

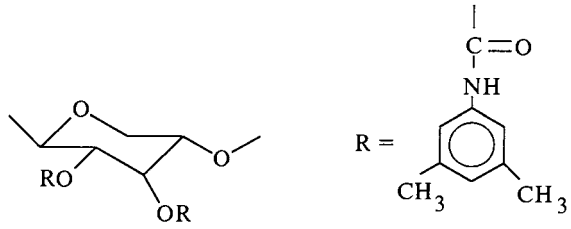
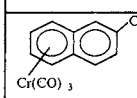
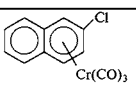
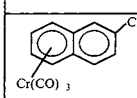
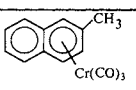
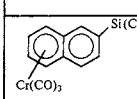
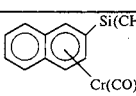
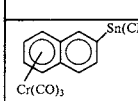
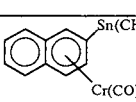
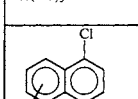
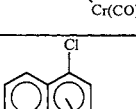
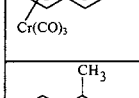
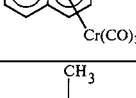
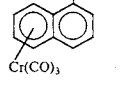
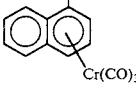
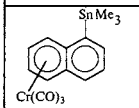
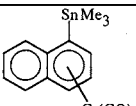


Fig. 1.

First, the possibility of separating racemates of chromium tricarbonyl complexes of α- and β-substituted naphthalenes by means of chiral phase HPLC on a chromatographic column packed with 3,5-dimethylcarbamate derivative of cellulose (Chiracell OD) was investigated. It should be noted that the effect of the $Cr(CO)_3$ group is very similar to the electron-withdrawing ability of an NO_2-substituent in an aromatic ring [22], so the use of the above-mentioned π-donor chiral

Table 1
HPLC separation of the enantiomers of chromium tricarbonyl complexes of substituted naphthalenes on Chiracel OD [a]

Complex	t_1,min	t_2,min	α	Complex	t_1,min	t_2,min	α
	13.32	14.00	1.07		9.65	10.35	1.11
	11.30	11.30	1.00		11.53	12.32	1.09
	7.33	8.66	1.33		6.00	14.66	4.27
	8.65	10.64	1.37		6.53	20.00	5.23
	12.00	17.37	1.62		10.00	14.30	1.65
	12.2	14.69	1.28		11.66	18.00	1.76
	7.34	8.00	1.16		8.53	15.20	2.29
	6.26	8.06	1.62		6.66	9.35	1.81

[a] $t_0 = 3.35$ min is the retention time of 1,3,5 tri-*tert*-butylbenzene as the non-retained compound from column passport. t_1 and t_2 are the retention times of the first and the second eluted enantiomer, respectively. Selectivity factor $\alpha = t_2 - t_0 / t_1 - t_0$.

phase column should provide a better enantioselectivity in the separation of arene tricarbonylchromium compounds. The results on retention and enantioselectivity of separation are presented in Table 1.

Some observations can be made from these data. The chromium tricarbonyl complexes of substituted naphthalenes having both $Cr(CO)_3$ and an electron-donating substituent ($-Si(CH_3)_3$, $-Sn(CH_3)_3$, $-CH_3$) in the same aromatic ring were more strongly retained than naphthalenes having these groups in different aromatic rings. Conversely, naphthalenes with two electron-accepting substituents ($Cr(CO)_3$ and –Cl) in one aromatic ring are more weakly retained than related naphthalene isomers having these substituents in different aromatic rings. This underlines the complicated character of the $\pi-\pi$ interaction between the chromium tricarbonyl complexes of naphthalenes and 3,5-dimethyl carbamate cellulose in the retention and separation of enantiomers of these organometallic compounds.

In general the enantioselectivity was higher for chromium tricarbonyl complexes of naphthalenes having an electron-donating substituent in the aromatic rings. In all cases, the enantiomers of β-substituted naphthalene complexes with $Cr(CO)_3$ exibit better resolution than related α-substituted compounds.

The increased volume of the electron-donating β-sustituent in naphthalenes has a tremendous effect on the improvement of enantioselectivity in the chromatographic separation. An extremely high value of enantioselectivity ($\alpha = 5.23$) for the bulky $Sn(CH_3)_3$-substituted complex (see Table 1) was achieved. The same trend, though less pronounced, was valid for the α-substituted naphthalene complexes with electron-donating substituents. Analysis of α values showed that unprecedented enantioselectivity was achieved, since for chromium tricarbonyl complexes of arenes it was previously been reported as $\alpha \leq 1.5$ [16]. Pure enantiomers of complexes were collected after a number of chromatographic runs on the Chiracel OD column under the above conditions and used for further incubation experiments.

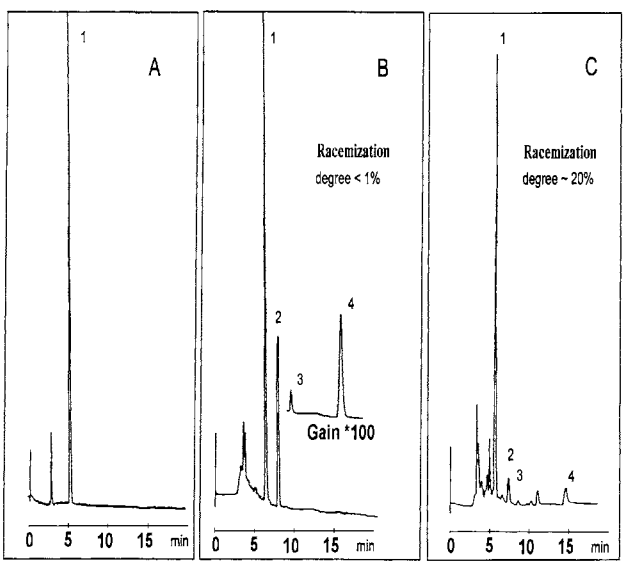


Fig. 2. Influence of organic solvent nature on the enantiomerization of chromium tricarbonyl complexes of 2-trimethylsilylnaphthalene during their haptotropic rearrangements **I** ⇌ **II**. Chromatograms: (A) pure enantiomer 1 of the structure **II** separated by HPLC on Chiracel OD; (B) enantiomer of structure **II** heated at 85°C for 40 h in C_6F_6; (C) enantiomer of structure **II** heated at 85°C for 40 h in toluene. Peaks: 1 and 4, enantiomers of structure **II**; 2 and 3, enantiomers of the structure **I**.

To deduce the mechanism of the metallotropic rearrangement, IRHR in different solvents (decane, C_6F_6, toluene) was investigated at 85°C for a number of optically pure complexes of substituted naphthalene, followed by chromatographic enantiomeric analysis of products. Typical results for chromium tricarbonyl complexes of β-trimethylsilylnaphthalene in C_6F_6 and toluene are presented in Fig. 2.

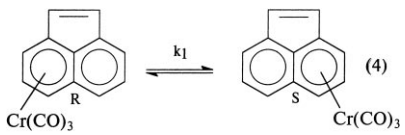
First, IRHR for optically the pure chromium tricarbonyl complex of the quite stable and less retained enantiomer of β-trimethylsilylnaphthtalene isomer of type **I** in C_6F_6 was investigated (Fig. 2(A)). Only two peaks for the reaction product corresponding to the equilibrium **I** ⇌ **II** (Fig. 2(B)) can be seen.

The lack of racemization ($\leq 1\%$) for both of these complexes in C_6F_6 proved that in non-solvating solvents IRHR proceeds intramolecularly (Fig. 2(B)). The same results were also obtained using decane. Similar incubation of the same enantiomer in toluene at 85°C leads, however, to ca. 20% loss in optical purity (Fig. 2(C)). We failed to observe IRHR **I** ⇌ **II** under the same conditions with the addition of 5% of THF to C_6F_6, due to the complete decomposition of the complex under the conditions of incubation (85°C, 40 h).

Preliminary results have shown that in the presence of even 50% of dibutyl ether in C_6F_6, complexes are more stable than in the presence of THF. Under these conditions it was observed that IRHR was accompanied by considerable racemization ($> 90\%$).

To our knowledge, it is the first time optically pure organometallics have been used for the investigation of IRHR. This approach has considerable promise not only for understanding the mechanisms of organometallic reactions but also for determining kinetic and thermodynamic parameters of degenerate rearrangements of some complexes with planar chirality. For example, in their pioneering work Hoffmann and co-workers theoretically predicted a considerable increase in the rate constants for the IRHR of the complexes of polycyclic aromatics with exocyclic double bonds, but the authors failed to determine this experimentally for chromium tricarbonyl of acenaph-

thylene by dynamic NMR [8]. It is quite clear that the rate constant of racemization of optically pure η^6-acenaphthyleneCr(CO)$_3$ is equal to the rate constant of the corresponding degenerate IRHR (Eq. (4)). Similarly, the rate constant of racemization for the pure enatiomer of η^6-indeneCr(CO)$_3$ corresponds to the rate constant for the sigmatropic [1,5]H-shift (Eq. (5)), which was determined only for some methyl-substituted chromium tricarbonyl complexes of indene [23]. This research is now in progress and results will be published later.



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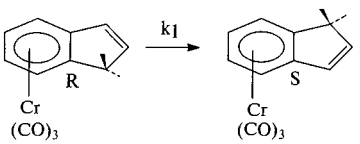

(5)

3. Experimental

3.1. Synthesis of materials

Chromium tricarbonyl complexes of monosubstituted naphthalenes were synthesized as described in Ref. [5] and were recrystallized in pure form from the benzene–heptane mixture before use.

3.2. Equipment and columns employed

A Laboratorny Pristroje (Prague, Czech Republic) liquid chromatograph with syringe pump, and a UV–vis photometric detector were used. Detection was performed at 254 nm. A Chiracel OD column (250 × 4.6 mm) was purchased from Daicel (Japan). The flow-rate of the mobile phase was 1.0 ml min^{-1}. The mobile phase was 9:1 *n*-hexane–2-propanol (v/v).

3.3. Incubation procedure

Complexes separated by means of HPLC were transferred to glass tubes and the mobile phase was evacuated at 10^{-5} mm. Tubes were filled with argon and the appropriate solvent added. Preliminary solvents were thoroughly freed of water and oxygen by storage on a potassium mirror, distillation and three consecutive freeze–pump–thaw cycles at 10^{-5} mm. All solvents and solvating additives (decane, ether, dibutyl ether, THF) prior to degassing were purified by refluxing over K–Na alloy and distilled under argon.

4. Conclusions

1. Chromium tricarbonyl complexes of a number of substituted naphthalenes have been effectively separated as their enantiomers by HPLC on a Chiracel OD optical column.
2. Optically pure isomers of chromium tricarbonyl complexes of substituted naphthalenes undergo IRHR by two possible mechanisms: intramolecular and dissociative (intermolecular). In inert non-solvating solvents this reaction proceeds via the intramolecular mechanism, whereas in aromatic solvents (toluene) this reaction proceeds through mainly an intramolecular mechanism but with considerable (15–20%) contribution from the dissosiative mechanism.
3. Hexafluorobenzene was found to be an optimal solvent for the investigation of intramolecular IRHR in transition metal complexes of polycyclic aromatics.
4. Investigation of the loss or retention of enantiomeric purity during organometallic reactions shows great promise not only for the understanding of mechanisms but also in determining kinetic and thermodynamic parameters of degenerate organometallic reactions.
5. We are continuing these experiments with other solvating additives (ether, dibuthyl ether, crown ethers etc.) and the results will be published elsewhere.

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